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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Confirmation No. 8625

Hanqing LIU

Group Art Unit 1742

Serial No. 10/667,883

Examiner Marcantoni

Filed: September 23, 2003

For: SELF-REDUCING, COLD-BONDED PELLETS

RESPONSE

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This is in response to the Office Action mailed July 8, 2004.

Claims 1-32 are rejected under 35 U.S.C. 102(a) and (b) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over Nayak et al '865 B2 or IN 171194 (Bandyopadhyay et al). The Examiner states that both references teach a pellet containing Portland cement clinker and other components that are the same as those claimed by the instant invention and thus anticipate the instant invention. Even if not anticipated, the Examiner concludes overlapping ranges of amounts would have been *prima facie* obvious to one of ordinary skill in the art. Further, the Examiner remarks the process of the claimed invention would appear to teach the same overlapping parameters and mixing of the same components. These rejections are respectfully traversed.

Prior to discussing the prior art, the present invention will be briefly reviewed. The present invention relates to self-reducing, cold-bonded pellets used in the ferrous industry and their process of production. Because of the self-reducing properties of the pellets when the cold-bonded pellets are heated to high temperatures, iron and steel can be more efficiently produced using the pellets and the pellets can be used in most smelting furnaces such as electric arc furnaces ("EAFs"), converting furnaces, open-hearth furnaces for steelmaking, blast

furnaces, non-blast furnaces for iron-making, and direct reduction iron (“DRI”) furnaces for producing DRI products.

The self-reducing, cold-bonded pellets comprise iron ore concentrate, carbonaceous reducing agent, and finely divided Portland cement clinker with special requirements as binder. The pellets’ components are about 60-79% by weight of iron ore concentrate, about 10-26% by weight of carbonaceous reducing agent, and about 10-20% by weight of finely divided Portland cement clinker with a special requirement as a binder, with the total weight being 100%.

The binder components are combined together to form a mixture. Pellets are produced when the mixture is placed into a balling disc or rotating drum and water is added. Pellets with predetermined size normally ranging from 8-16 mm are obtained by using roller screens. The pellets are then continuously placed into a curing device. Inside the curing device, the pellets will be hydrated and carbonated by using hot gases containing carbon dioxide with a temperature range of about 100-300 °C. Thereafter, after drying, the dried pellets are discharged from the curing device and will be ready for use.

The pellets will keep their original structure which will prevent them from cracking and pulverizing at high temperature in the preheating environment and the steelmaking furnace. By using the high quality binder, the optimal design and the special creative manufacturing process, the self-reducing cold-bonded pellets can be produced with high strength both at room temperature and high temperature. Before the separation between the slag and liquid iron, the pellets will retain their original shape when the pellets are heated to a high temperature.

When the pellets are put into molten steel, and because of the high temperature, carbon inside the pellets gasifies completely; molecule moves very actively and the reduction rate is very high. Thus, the reduction of iron ore in these kinds of pellets can be finished in no more than 3 minutes after preheating at high temperature and then the pellets will be melted.

The prior art cited by the Examiner does not anticipate or suggest the present invention. The Nayak et al invention relates to a process for manufacture of high iron hydraulic cement clinker in production of cement and cementation binder for application in construction activity and in metallurgical industry for sintering of iron ore fines and making cold bonded briquettes and pellets.

High iron cement clinker in Nayak et al is a non-Portland type of cement clinker which contains iron ( $\text{Fe}_2\text{O}_3$ ) to the extent of 40% and above as a major chemical constituent. The cement made from high iron cement clinker possesses high binding strength on hydration. This

type of high iron hydraulic cement is usable as a substitute to Portland cement in construction, a special cement in sulphate resistance constructions, a metallurgical cement or a binder in briquetting, pelletization and sintering of iron ore, iron oxide and metal containing fines for iron making and a hydraulic mineral binder for absorbing water-soluble metals in the treatment and stabilization of hazardous toxic solid wastes. Chemically and mineralogically, the high iron cement is quite different from the Portland and aluminous cements.

The Nayak et al process for the manufacture of a high iron hydraulic cement clinker uses a down-draft sintering technique which comprises preparing a homogenous raw mixture of raw materials, pelletizing the resultant homogenized raw mixture in the presence of water to prepare granulated particles, sintering and cooling the pelletized granulated particles by a down-draft sintering technique to convert into clinker, grinding the clinker particles with and without gypsum to make high iron hydraulic cements and binders for different applications.

The drying by calcination, sintering and then cooling of the material to form the cement clinker takes place on a static bed. The presence of solid carbon within the charge material generates *in-situ* heating to provide a temperature ranging from 1000 to 1500° C or higher in the bed. Conversion of the charged bed into cement clinker takes about 15 to 30 minutes of time depending on the height and permeability of the charge bed, the air suction pressure, the sintering temperature, etc. The clinker product discharged from the sinter pot is crushed to below 10 mm for storage or ground to make cement.

Nayak et al proposes a process for the manufacturing of high iron hydraulic cement clinker, but does not state how to produce cold-bonded pellets. The final product is a type of cement clinker, not an iron ore pellet for use in metallurgy. The cement clinker principally relates to the cement industry.

In the process for producing this type of high iron hydraulic cement clinker, the granulated particles containing  $\text{Fe}_2\text{O}_3$  (less than 40%), solid carbon (4-12%) and other materials are prepared by pelletizing.  $\text{Fe}_2\text{O}_3$  contained in the particles is not used for iron producing. It is used for forming ferrite mineral phases ( $\text{C}_2\text{F}$ ,  $\text{C}_4\text{AF}_2$ ,  $\text{C}_6\text{AF}_2$ ,  $\text{C}_6\text{A}_2\text{F}$ ). The solid carbon contained in the pelletized granules is not used as a reducing agent; it is used for generating heat for clinker formation.

Most importantly, the pellets in Nayak et al do not contain Portland cement clinker as in the present invention. In fact, Nayak et al clearly distinguishes the high iron hydraulic cement from Portland cement.

This high iron hydraulic cement clinker is said to be suitable for application in metallurgical industry as well as the sintering of iron ore fines and making cold bonded briquettes and pellets. However, there is no description of the pellets that use this high iron hydraulic cement clinker as a binder or any information about its pellet properties which would indicate that it is suitable for use in the metallurgy industry for iron-making or steelmaking.

If the high iron cement clinker could be used as a binder to manufacture pellets with a high cold compressive strength, there is no indication the pellets would have good high temperature performance as required for a successful use as a charge for blast furnaces in metallurgy industries.

IN 171194 discloses a process for producing high-strength cold-bonded ore pellets of ore fines having a strength of 200 kg/pellet. These pellets are made of ore fines (80-90%) and Portland cement clinker (7-10%) and accelerator (0.4-2.8%). The accelerator consists of  $\text{CaCl}_2$  and/or Ca formate. In the curing process, the pellets are heated for 2-4 hours at 40-90° C, hardened in steam for 3-10 hours at 5-40 psi, and heated further for 2-40 hours at 80-200° C for drying. The pellets are of 15-20 mm diameter and have a crush strength of nominally 200 kg/pellet. The pelletizing process is suitable for the ores of Fe, Cr, or Mn.

These pellets do not contain the carbonaceous reducing agent (e.g., coal powder) of the present invention, so they do not possess the important property of self-reducing. This property is very important when using the pellets as a charge for greatly reducing the coke ratio in blast furnace iron-making, and this is also important in realizing direct steelmaking.

The content range of Portland cement clinker is 7-10%. This differs from the 10-20% binder content range stated in the present application.

The pellets also do not have the special technical requirements as in the Portland cement clinker of the present invention, and this will result in the cement properties of the binder having great differences and cause the pellets' quality to become highly unstable. This Indian patent tries to solve the problem by adding the accelerator  $\text{CaCl}_2$  to the pellet to increase early strength. In contrast, the present invention does not need any accelerators because of the special required Portland cement clinker.

The pellets are not cured with carbon dioxide gases in the Indian patent and the curing steps include first preheating, then hardening in steam at 5-40 psi and finally heating further for drying. The hot strength of the pellets cured with a steaming process is lower than pellets cured with a combination of hydration and carbonation as in the present invention. In addition, in

applicant's opinion, it is difficult to realize continuous industrial production if the pellets are cured by high-pressure methods.

The pellets of 15-20 diameter have a high crush strength of nominally 200 kg/pellets. The reason why former cold-bonded pellets could not take the place of sinter as a charge in the blast furnace is mainly because their high temperature metallurgical properties could not meet the application needs.

The reason why cold-bonded pellets using cement or cement clinker as a binder in the past could not be applied widely in industry production is because the characteristic properties of the cement or cement clinker have not been sufficiently studied and because the main factors affecting the pellet properties have not been fully explored.

Because the key problem in seeking a suitable binder for producing high quality self-reducing pellets has been solved by the present invention, and also because the carbon content of the pellet and the industrial process of hydration and carbonation have been properly designed, the current self-reducing pellets are superior to former pellet technology.

Due to the specially required Portland cement clinker as binder and the properly designed processes, the resulting pellet quality is extremely stable and continuous industrial production can be realized:

1. the pellets have self-reducing properties;
2. the pellets have a quick reduction speed;
3. the pellets possess higher hot strength, no cracking or pulverizing while heating and reducing;
4. the properties of the pellets can be adjusted in accordance with different smelting requirements by adjusting coal and /or binder; and
5. the pellet containing coal or coke breeze can completely replace sinter as a blast furnace charge, greatly reducing the coke ratio by up to 280 kg/t. The pellet can also be used as a charge for iron-making in non-blast furnaces, for DRI production and for direct steel-making, greatly reducing both power consumption and production costs.

Industrial experiments have showed that only the special required Portland cement clinker can meet the specifications required for producing the self-reducing pellets in the present invention.

The performances of Portland cement clinker are mainly decided by the mineral contents of tricalcium silicate ( $\text{Ca}_3\text{S}$ ), dicalcium silicate ( $\text{Ca}_2\text{S}$ ), tricalcium aluminate ( $\text{Ca}_3\text{A}$ ), brown

millerite ( $\text{Ca}_4\text{AF}$ ) and free lime ( $\text{f-CaO}$ ). The mineral contents of cement clinker produced by different cement kilns are normally dissimilar due to the differences of materials, processes, equipment and/or operations. Generally, the mineral contents are as follows:  $\text{Ca}_2\text{S}$ =15-37%,  $\text{Ca}_3\text{S}$ =37-60%,  $\text{Ca}_3\text{A}$ <15%,  $\text{f-CaO}$  < 4%. Even with one and the same cement kiln, mineral content of the clinker varies at any moment in operation. So, the selection for the required Portland cement clinker should be made while in operation of the cement kiln if its clinker is to be used as the bonding agent for the pellets.

$\text{Ca}_2\text{S}$  has the lowest hydration speed compared with other minerals in the Portland cement clinker. At 20° C, only 1% of  $\text{Ca}_2\text{S}$  can be hydrated in 24 hours, whereas 36% of  $\text{Ca}_3\text{S}$  can be hydrated within that same time. And while at 90° C, in the same 24-hour period, compared with only 22% of  $\text{Ca}_2\text{S}$ , 90% of  $\text{Ca}_3\text{S}$  can be hydrated in that same amount of time. Quick hydration is the precondition of carbonation in the curing process because calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is produced from the hydration of the minerals. The more calcium hydroxide produced from the hydrated clinker, the better the carbonation of pellets. The early strength of green pellets also depends on the hydration of such minerals.

For the basic requirements of the cement clinker as a binder, the  $\text{Ca}_2\text{S}$  content must be less than 20% by weight. At this time, the  $\text{Ca}_3\text{S}$  content should be more than 50%, because  $\text{Ca}_2\text{S}$  and  $\text{Ca}_3\text{S}$  are normally about 70% by weight. The Portland cement clinker with the basic requirements is suitable as a binder for the applications that do not need higher pellet strength, e.g., for DRI productions. For the blast furnace, the  $\text{Ca}_3\text{S}$  content should be at least 56%, or for even better results, above 60%, while at this time  $\text{Ca}_2\text{S}$  content should be far lower than 20%. In addition, the ratio of  $\text{Ca}_3\text{S}$  and  $\text{Ca}_3\text{A}$  should be controlled between 5 and 10.

The pellets produced without using special required Portland cement clinker as binder will not be fully hydrated and carbonated in industrial conditions. This will cause the pellets to have lower strength and poor high temperature performance, resulting in easily cracked and pulverized pellets. In industrial production, the off-grade binder may cause the pellets to stick to each other and hang up while in the curing device, or even cause all of the pellets to become bonded in a firm mass. The pellets produced with off-grade binder will cause irregular blast-furnace performance or stiff furnace operation. So, the common Portland cement clinker without special requirements cannot be used as binder for manufacturing the self-reduced pellets in the present invention.

In the present invention, the fact that a lot of iron is reduced in the pellets at high temperature results in the pellets having a high hot strength. The fixed carbon content should have a value where at least 90% of iron is reduced from the total oxidic iron contained in the pellet so as to have more than enough iron to form a firm connection.

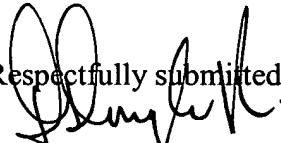
Other important factors affecting the pellet properties are the pelletizing process, the hydration and carbonation process, and also some conditions of iron ore or coal. All the factors should be comprehensively considered before the success can be realized in industrial production and utilization of pellets.

It is becoming vitally important to reduce iron efficiently from iron ore so as to lower pollution in modern steel industry. The present invention will help make great progress in this area.

In view of the foregoing, early and favorable action is respectfully requested.

The Commissioner is hereby authorized to charge any fees in connection with the present Response to Deposit Account 19-4293.

Respectfully submitted,



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